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UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARO 18522.7-CH	2. GOVT ACCESSION NO. N/A	3. RECIPIENT'S CATALOG NUMBER N/A
4. TITLE (and Subtitle) An Ultrasensitive and Element Specific Photoionization Detection System for Environmental Analysis		5. TYPE OF REPORT & PERIOD COVERED 18 Jan 82 - 17 Jan 85 Final Report 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Albert Zlatkis		8. CONTRACT OR GRANT NUMBER(s) DAAG29-82-K-0054
PERFORMING ORGANIZATION NAME AND ADDRESS University of Houston		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE Mar 85 13. NUMBER OF PAGES 5
MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Photoionization	Gas Chromatography
Environmental Analysis	Photoionization Detecots
Chemical Detection	Hydrogen Sulfide
Ammonia	Phosphine
Phosphorus	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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20. ABSTRACT CONTINUED:

their determination by gas chromatography. The photoionization detector (PID) now commercially available is capable of providing the very high sensitivity desired for trace level analysis. Indeed its low volume ionization chamber make it suitable for use with capillary columns. The PID also lends itself to the development of an element selective detector. This could be expected by catalytic conversion of the effluent to H_2S, PH_3, and NH_3. Scrubbers to remove unwanted gases could yield e.g. PH_3 only thereby making the detector P selective. Sensitivities at the pg level could be possible.

ARO 18522.7-CH

AN ULTRASENSITIVE AND ELEMENT SPECIFIC PHOTOIONIZATION DETECTION SYSTEM FOR ENVIRONMENTAL ANALYSIS

FINAL REPORT

Albert Zlatkis

March 15, 1985

U.S. Army Research Office

Contract No. DAAG-29-82-K-0054

University of Houston - University Park

Houston, Texas

AN ULTRASENSITIVE AND ELEMENT SPECIFIC PHOTOIONIZATION DETECTION SYSTEM FOR ENVIRONMENTAL ANALYSIS

Statement of the Problem

The problem of trace analysis at the parts per trillion level in environmental samples has been a challenging one for analytical chemists during the past two decades. The presence of substances in very low concentrations in a complex matrix demands the development of both selective and sensitive detectors for their determination by gas chromatography. The photoionization detector (PID) now commerically available is capable of providing the very high sensitivity desired for trace level analysis. Indeed its low volume ionization chamber make it suitable for use with capillary columns. The PID also lends itself to the development of an element selective detector. This could be expected by catalytic conversion of the effluent to H_2S, PH_3, and NH_3. Scrubbers to remove unwanted gases could yield e.g. PH_3 only thereby making the detector P selective. Sensitivities at the pg level could be possible.

Additional keywords: chemical detection; ammonia, phosphorus; phosphine.

Summary of Most Important Results

1. The design and construction of an "on-column" for injector capillary columns. This system permitted the direct injection of 1-100 µL liquid samples into capillary columns of 0.25mm I.D.

2. The development of a system for injecting 100 µL liquid samples into a capillary column containing a bonded stationary phase. By permitting the solvent to pass through the column as a liquid, the trace impurities were left adsorbed on the stationary phase. Thermal desorption, focusing in the last 15 cm of the column at liquid nitrogen temperatures, then temperature programming into a second capillary column yielded excellent chromatograms and analysis at the ppb level. This system is compatible with both flame ionization and photoionization detectors.

3. The use of the electron capture detector with the system discussed in (2.) to determine halogenated compounds e.g. lindane at a level as low as 5 parts per trillion in aqueous samples.

4. The modification of a comerically available PID to make it compatible with fused silica bonded phase capillary columns.

5. The development of a microcatalytic converter to pyrolyze the eluent from a gas chromatographic system to water, methane and other compounds depending on the functional groups present. Pyrolysis and reduction were effected by hydrogen and nitrogen (80:20) as the carrier gas. Heterogeneous catalysis was achieved by using 1% Pd on Chromasorb W. This material was prepared by dissolving $PdCl_2$ in 5% solution of acetic acid in water. The dried material was heated at 300° under hydrogen for 16 hours in quartz tubing (10 cm x 0.5 cm id.). Model compounds tested were diethyl sulfide, carbon disulfide, acetonitrile, pyridine and trimethylphosphine. Reduction pyrolysis of these compounds formed H_2S, NH_3, and PH_3. The use of sulfur compounds limited the

life of the catalyst. The nitrogen and phosphorus compounds did not effect the catalyst. Alumina was used as the scrubber to remove any unwanted phosphine. Sensitivities were in the nanogram range. Further increments of sensitivities may be possible by using ultrapure carrier gases.

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Participating Personnel

H. Shanfield

K. Kim - Post doctoral fellow

F.-S. Wang - Ph.D earned during this period

L. Ghaoui - Ph.D earned during this period

A. Lochner